

CD221. LECTURE 8. THE IDEAL GAS.

The basic methodology of the statistical mechanical formalism should now be fairly clear – it consists in finding the number of microstates of a system Ω that are compatible with definite values of a specified set of macroscopic variables, like the energy U , the volume V , the length L , or the number of particles N , and then linking Ω to thermodynamics through the Boltzmann equation. We'll now consider one last system to which this methodology can be quite easily applied – the ideal gas.

The ideal gas is a collection of N independent, non-interacting indistinguishable point particles that are confined to a box of volume V and that only possess translational (i.e., kinetic) energy. (Note that we are now no longer assuming – as we had at the beginning of these lectures – that individual particles can be distinguished from each other.) It is a very good model of real gases at high temperatures and low densities, and we already know quite a bit about it at the thermodynamic level. In particular, we know that its mechanical equation of state is given by

$$PV = Nk_b T \quad (1)$$

But why should a collection of such particles obey this particular equation, and is there a way to arrive at it from a knowledge solely of a *single* particle's microscopic properties? What we presently know (from quantum mechanics) about a single point particle that's confined to the inside of a 3-dimensional cubical box is that it's *not* free to move around with any energy it likes; it can only do so with certain *special* energy values. (This was the case with isolated harmonic oscillators too, as we saw earlier.) These special values (called eigenvalues) are given by the formula

$$\varepsilon_{jkl} = \frac{h^2}{8mL^2} (j^2 + k^2 + l^2), \quad j, k, l = 1, 2, 3, \dots, \infty \quad (2)$$

where h is Planck's constant (the appearance of which is a sure sign that we're in the quantum realm), m is the mass of the particle, L is the length of a side of the box, and j , k and l are quantum numbers, which are restricted to being integers. (As before, we'll accept Eq. (2) as a true description of particle behavior at the microscopic level, without worrying about where it comes from.)

A particle obeying Eq. (2) is said to be in a definite energy state when each of the 3 quantum numbers in this equation has a definite value. If there were any other particle in the box, its energy would also be determined by Eq. (2) (since we've assumed that the particles are independent and non-interacting), but in general it would be characterized by j , k , l values that were different from those of the first particle. This remains the case no matter how many particles are in the box. This means that for a system of N such particles, the total energy U will be

$$U = \frac{h^2}{8mL^2} \sum_{i=1}^N (j_i^2 + k_i^2 + l_i^2), \quad j_i, k_i, l_i = 1, 2, 3, \dots, \infty \quad (3)$$

We can think of this system as being in a *macrostate* characterized by U , N and L and in *microstate* characterized by $j_1, k_1, l_1, j_2, k_2, l_2, \dots, j_N, k_N, l_N$ in which each particle has definite values for each of its 3 quantum numbers. Clearly, there can be a number of different *combinations* of these $3N$ quantum numbers that satisfy Eq. (3). In general, then, there will be a number of different microstates that correspond to this particular macrostate.

What we would like to do now is calculate this number, which is of course nothing but Ω (which up to this point we've been calling the multiplicity, but which we'll now begin referring to as the *microcanonical partition function*.) Since it's not immediately obvious how to proceed, let's first attempt the calculation of Ω for a simpler case: a *single* particle in a 2-dimensional box. For this system, Eq. (3) reduces to

$$U = \frac{h^2}{8mL^2} (j^2 + k^2), \quad j, k = 1, 2, 3, \dots, \infty \quad (4)$$

By introducing the definition $R^2 \equiv 8mL^2U / h^2$, we can write Eq. (4) more compactly as

$$R^2 = j^2 + k^2, \quad j, k = 1, 2, 3, \dots, \infty \quad (5)$$

(which is of exactly the same form as the equation of a circle of radius r , viz., $r^2 = x^2 + y^2$.) We can exhaustively enumerate the various microstates of this system by listing all the values of j and k that when substituted into Eq. (5) produce a particular value of R . The listing of j and k can be done graphically, by plotting their values along two perpendicular axes, as shown. Each point in this graph represents a microstate of the system. A few such states are illustrated below, including, specifically, (1,1), (3,1) and (1,3).

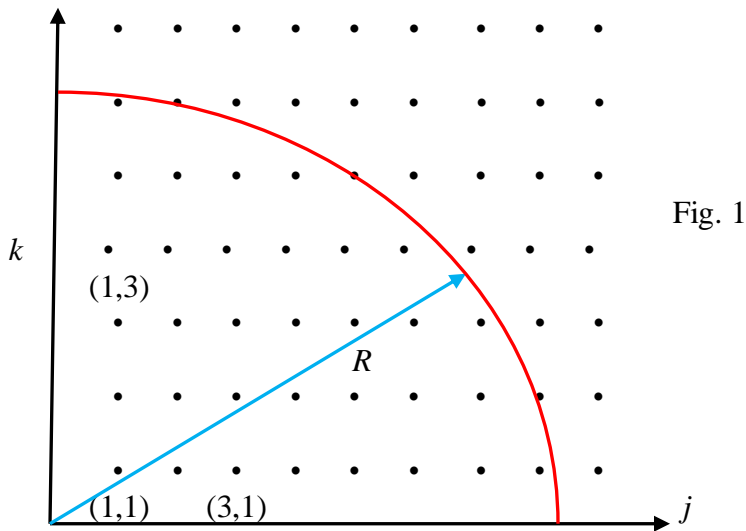
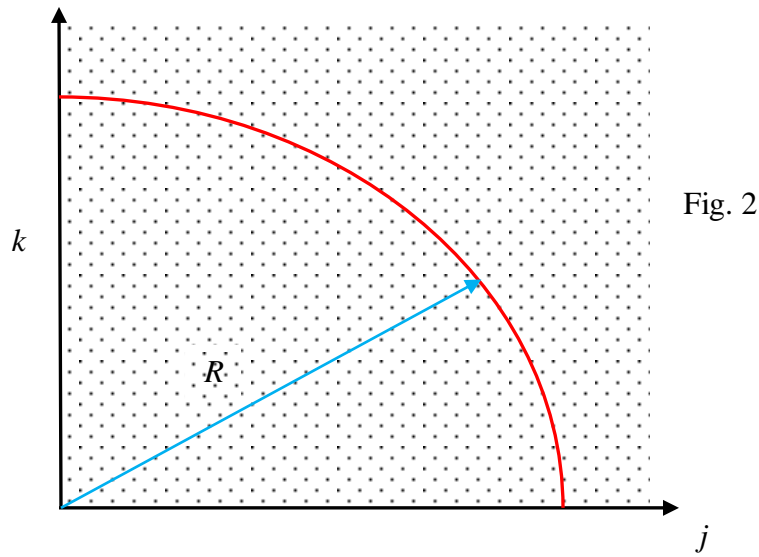


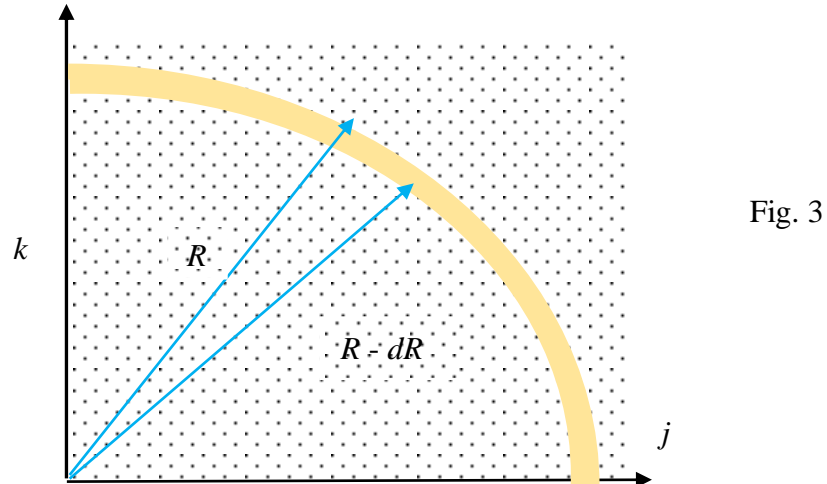
Fig. 1

But only a subset of these states satisfy Eq. (5). The states that do are those that intersect the red line in Fig. 1, which is the arc of a circle of radius R centered at the origin whose locus is defined by the equation $R^2 = j^2 + k^2$, (j and k being assumed continuous for the purpose of drawing the curve.)

In the example of Fig. 1, very few states actually meet the curve, but that's only because we're considering small values of j , k and R . In real systems (i.e., real gases), these numbers would be much much larger. For instance, for an N_2 molecule in a 1-d box at room temperature (300 K), the average energy U is about 2×10^{-21} J (by equipartition). If the length of the box, L , is taken to be 1 cm, the formula $U = h^2 j^2 / 8mL^2$, with the mass m estimated to be 5×10^{-23} gm, gives a j value on the order of 10^9 , which means that for real systems, Fig. 1 will look more nearly like this:



That is, effectively, j and k vary continuously, and the area under the curve in Fig. 2 is basically the number of microstates lying *below* R . We can then *approximate* the number of microstates Ω lying *on* R by the area of a thin band lying between R and $R - dR$, where dR is the width of the band. This area is the shaded region shown in Fig. 3 below:



In estimating Ω by an *area* between two arcs rather than by the *length* of an arc, we're tacitly acknowledging that in the laboratory we can't really measure energy with absolute precision – there's always some spread in its value because of experimental uncertainty.

The area of the shaded portion in Fig. 3 – Ω , in other words – is easily calculated; it is

$$\begin{aligned}
 \Omega &= \frac{1}{2^2} \left[\pi R^2 - \pi (R - dR)^2 \right] \\
 &= \frac{1}{4} \left[\pi R^2 - \pi R^2 \left(1 - \frac{dR}{R} \right)^2 \right] \\
 &\approx \frac{1}{4} \left[\pi R^2 - \pi R^2 \left(1 - 2 \frac{dR}{R} + \dots \right) \right] = \frac{\pi R dR}{2}
 \end{aligned} \tag{6}$$

Knowing the connection between R and U (and L), Eq. (6) can be translated into an expression for the number of microstates of a single particle having energy U in a box of length L .

If the same particle were in a box of 3 dimensions, its energy would be

$$U = \frac{h^2}{8mL^2} (j^2 + k^2 + l^2), \quad j, k, l = 1, 2, 3, \dots, \infty \tag{7}$$

or, in terms of R ,

$$R^2 = j^2 + k^2 + l^2, \quad j, k, l = 1, 2, 3, \dots, \infty \tag{8}$$

which is the equation for the surface of a sphere (again, taking j , k and l to be continuous, which at high quantum numbers, they practically are.) The area of this surface provides an estimate of the number of states Ω satisfying Eq. (7).

In analogy with the 2-D case, we can approximate this number as

$$\Omega = \frac{1}{2^3} (\text{Volume of sphere of radius } R - \text{volume of sphere of radius } R - dR) \tag{9}$$

Schematically, the RHS of Eq. (9) corresponds to the region in red in Fig. 4 below:

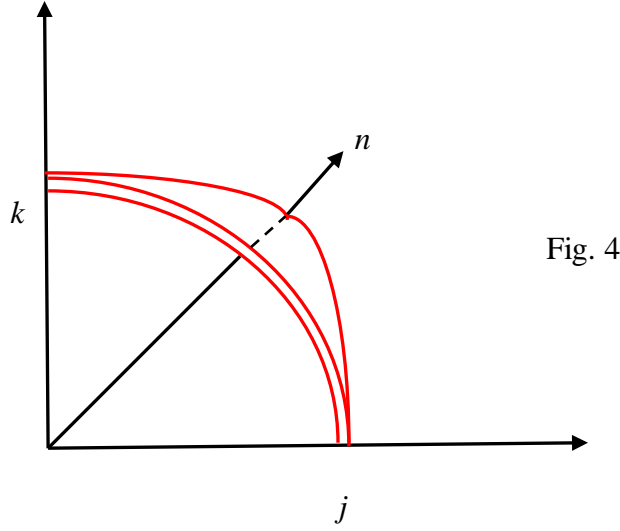


Fig. 4

The factor of 8 in Eq. (9) accounts for the fact that j , k and l are all positive, so only that part of the sphere that lies in the first quadrant of the coordinate axes is relevant to the calculation. Putting in the expression for the volume of a sphere in Eq. (9), we find that

$$\begin{aligned}
 \Omega &= \frac{1}{2^3} \left[\frac{4\pi R^3}{3} - \frac{4\pi(R-dR)^3}{3} \right] \\
 &= \frac{1}{8} \left[\frac{4\pi R^3}{3} - \frac{4\pi R^3}{3} \left(1 - \frac{dR}{R} \right)^3 \right] \\
 &\approx \frac{1}{8} \left[\frac{4\pi R^3}{3} - \frac{4\pi R^3}{3} \left(1 - 3\frac{dR}{R} + \dots \right) \right] = \frac{\pi R^2 dR}{2} \quad (10)
 \end{aligned}$$

The way to generalize this result to a system of N particles in a 3-d box is now clear. We start with

$$R^2 = j_1^2 + k_1^2 + l_1^2 + j_2^2 + k_2^2 + l_2^2 + \dots + j_N^2 + k_N^2 + l_N^2 \quad (11)$$

which is the equation for the surface of a “hypersphere”, this being a geometrical object that lives in an imaginary space defined by a coordinate system in which $3N$ axes, one for each of the $3N$ quantum numbers, intersect each other at right angles. With this definition we expect to be able to calculate Ω as

$$\Omega = \frac{1}{2^{3N} N!} [\text{Vol. of hypersphere of radius } R - \text{vol. of hypersphere of radius } R - dR] \quad (12)$$

Some words of explanation about this expression are in order. The factor of 2^{3N} ensures that only that part of the hypersphere that lies in the first “quadrant” of the generalized coordinate system is included, a restriction dictated by the positivity of the quantum numbers. The factor of $N!$ – introduced “by hand” – accounts (approximately) for the intrinsic indistinguishability of the particles. To see how this is achieved, consider a 3 particle system in 3-d. A typical microstate of this system could be represented as the “vector”

$$\mathbf{J}, \mathbf{K}, \mathbf{L}$$

where $\mathbf{J} = (j_1, k_1, l_1)$, $\mathbf{K} = (j_2, k_2, l_2)$ and $\mathbf{L} = (j_3, k_3, l_3)$. Any other microstate of the system that differed from this one only by a permutation of these 3 labels would not be a distinct microstate when the particles are indistinguishable. But in the foregoing approach to the calculation of Ω , such states, differing only by a permutation of the particle labels, would in fact be included in the overall count. This immediately apparent in the case of a 2 particle gas in 1-d, for which the energy equation is

$$R^2 = j_1^2 + j_2^2, \quad j_1, j_2 = 1, 2, 3, \dots$$

When the quantum numbers are plotted, and Ω is calculated from the area lying between two circular arcs, as shown

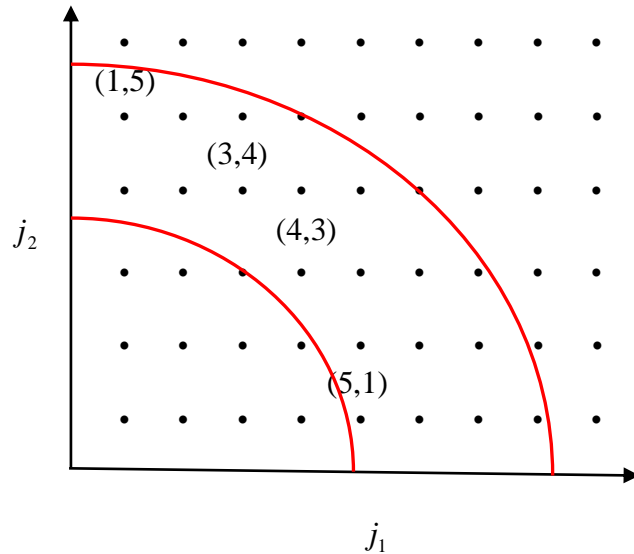


Fig. 5

we see that states like (5,1) and (4,3) are counted as distinct from (1,5) and (3,4) when they shouldn't be if the particles are truly indistinguishable. For this 2-particle system, division by $2!$ corrects for the double counting. In the same way, to correct for the same kind of over-counting in an N -particle system, we divide by $N!$.

But this correction is actually only approximate. The reason is that the present counting scheme (based on the area between two arcs) *doesn't* over-count certain other states. These states include those where all the particles happen to be in exactly the same energy state (and so have the same quantum numbers), like the state **J, J, J**, for instance, in the case of a 3 particle system in 3-d. This state is correctly counted just once, but by introducing the $N!$ correction factor, the contribution of this state to Ω is actually *under-counted*. It turns out, though, that this doesn't really matter, because when we deal with quantum numbers on the order of 10^9 , only a minuscule fraction of the relevant microstates are likely to share any of the same single-particle energy states.

With these considerations in mind, we can return to Eq. (12) to continue the calculation of Ω for an N -particle system in a cubical box. The calculation requires an expression for the volume of a hypersphere, V_{3N} , which happens to be known (we don't need to go into the details of the derivation here), and is given by

$$V_{3N} = \frac{\pi^{3N/2} R^{3N}}{\Gamma(3N/2 + 1)}. \quad (13)$$

Here the symbol $\Gamma(x)$ stands for a quantity called the gamma function. The gamma function is a generalization of the factorial function, and has the following integral representation:

$$\Gamma(x) = \int_0^{\infty} dt t^{x-1} e^{-t}, \quad (14a)$$

where x is any *real* number greater than -1 . The connection to factorials is made by noticing that when x is $n+1$, with n an *integer*, Eq. (14a) becomes $\Gamma(n+1) = \int_0^{\infty} dt t^n e^{-t}$, which then leads to $\Gamma(n+1) = n!$ after the RHS is evaluated using integration by parts (as in our derivation of Stirling's approximation.)

The gamma function has many interesting properties, of which the two most important for the present discussion are

$$\Gamma(x+1) = x\Gamma(x) \quad (14b)$$

and

$$\Gamma(1/2) = \sqrt{\pi} \quad (14c)$$

Returning again to Eq. (12), we see that when we substitute Eq. (13) into it we get

$$\begin{aligned}\Omega &= \frac{\pi^{3N/2}}{2^{3N} N! \Gamma(3N/2 + 1)} \left[R^{3N} - (R - dR)^{3N} \right] \\ &= \frac{\pi^{3N/2}}{2^{3N} N! \Gamma(3N/2 + 1)} R^{3N} \left[1 - \left(1 - \frac{dR}{R} \right)^{3N} \right]\end{aligned}\quad (15)$$

The second term in square brackets in Eq. (15) is a number less than 1, and it is raised to a huge power (a number on the order of 10^{23}), so it is effectively 0, and Eq. (15) therefore reduces to

$$\Omega = \frac{\pi^{3N/2} R^{3N}}{2^{3N} N! \Gamma(3N/2 + 1)} \quad (16)$$

This is the expression we were after, but we need to re-express it in terms of U , $V = L^3$ and N using the definition $R = (8mL^2U/h^2)^{1/2} = (8mV^{2/3}U/h^2)^{1/2}$. What we then end up with is

$$\Omega(U, V, N) = \left(\frac{2\pi m}{h^2} \right)^{3N/2} \frac{U^{3N/2} V^N}{N! (3N/2)!} \quad (17)$$

(We've replaced $\Gamma(3N/2 + 1)$ by $(3N/2)!$, which is a purely *formal* step since we don't know what the factorial of a fraction is, but we plan to apply to Stirling's approximation to Eq. (17), and that will get rid of all the factorials anyway.)

Equation (17) is the culmination of the statistical mechanical part of the calculation. It now remains to make the connection to thermodynamics using $S = k_B \ln \Omega$. When we do this and simplify the results with Stirling's approximation, we find that

$$S = \frac{5Nk_B}{2} + Nk_B \ln \left[\left(\frac{4\pi m}{3h^2} \right)^{3/2} \frac{U^{3/2} V}{N^{5/2}} \right] \quad (18)$$

This is the fundamental equation of the ideal gas, and it's known as the Sackur-Tetrode equation. It can be re-written in the form

$$S = Ns_0 + Nk_B \ln \left[\left(\frac{U}{U_0} \right)^{3/2} \left(\frac{V}{V_0} \right) \left(\frac{N}{N_0} \right)^{-5/2} \right] \quad (19)$$

which is how Callen writes it in Eq. (3.34).

Knowing the fundamental equation of a system means that we can now derive all of its thermodynamic properties. Specifically, applying $(\partial S / \partial U)_{V,N} = 1/T$ and $(\partial S / \partial V)_{U,N} = P/T$ to Eq. (18) (or (19)), we immediately arrive at

$$U = \frac{3}{2} N k_B T \quad (20a)$$

and

$$PV = N k_B T \quad (20b)$$

which, of course, correctly describe the properties of an ideal gas in the bulk. So again, statistical mechanics provides a microscopic route to the determination of macroscopic behavior.